REMARKS

Claims 1-3 remain pending after response.

Withdrawn Rejection

Applicants acknowledge with thanks the withdrawal of the previous rejection under 35 USC 112 (paragraph two).

Rejection under 35 USC 103(a)

Claims 1-3 stand rejected under 35 USC 103(a) as being unpatentable over Asahi et al '288 in view of Ichikawa et al '734. This rejection is respectfully traversed.

It is respectfully submitted that the Examiner is using hindsight reconstruction as a basis for alleging that a combination of the Asahi et al '288 patent with the Ichikawa et al '734 patent renders the claims obvious to one skilled in the art. Indeed, as acknowledged by the Examiner, neither of the cited references teach or suggest the claimed invention. Hence, it has been necessary for the Examiner to combine the teachings of the respective references in an attempt to arrive at the claimed invention. A review of the teachings of the respective references confirms that the references cannot be logically combined to result in the claimed invention, and the rejection is thus without basis.

Differences in Substrate and Reaction

Asahi teaches the use of an aromatic compound having an alkyl group or a partially-oxidized alkyl group as a substrate. By contrast, the Ichikawa reference teaches the use of an

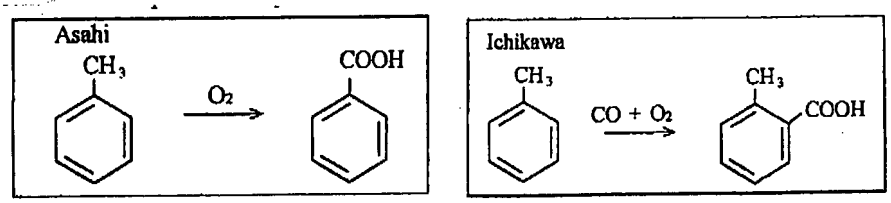
aromatic compound having at least one hydrogen atom directly attached to a carbon atom comprising the aromatic ring.

With regard to the substrates, an alkyl moiety actually participates in the reaction of Asahi. By contrast, in Ichikawa, the aromatic ring moiety participates in the reaction.

In Asahi, oxidation of the alkyl group is conducted to yield a corresponding carboxy compound. By contrast, in Ichikawa, the aromatic compound reacts with a carbon monoxide and molecular oxygen to yield a corresponding carboxy compound (see column 7, lines 3-8). For the record, in Ichikawa, the carboxylation reaction is the reaction in which the carbon number of the substrate is increased.

As noted by the Examiner, the aromatic compound used as the substrate in Ichikawa may have an alkyl group as a substituent. Therefore, it may appear that a common substrate is employed in both references. However, it cannot be considered that the references use a common substrate because the reaction sites differ from one another as discussed above. Consequently, the type of reaction and product material differ from one another.

For example, when toluene is used as a substrate in each reference, different products result in each. That is, though Asahi oxidizes methyl groups, Ichikawa introduces a carboxyl group which directly combines with a carbon atom making up the aromatic ring, and unreacted methyl group remains as noted by the following reaction schemes (which make clear such a distinction between the respective references):



As mentioned above, Asahi differs from Ichikawa with respect to all substrates, reaction schemes and resulting products. Therefore, one of ordinary skill in the art would lack any motivation to combine any teachings of Ichikawa with those of Asahi in the manner asserted by the Examiner.

In this regard, the Examiner takes the position that Ichikawa teaches the equivalency between the method of using carbon monoxide and oxygen, and that of using an oxygen-containing gas in the presence of a catalyst containing platinum chloride in introducing the carboxyl group to the aromatics based on column 1, line 61 to column 2, line 2. However, the reference cited in that portion of the reference (*Chem. Abstracts* 69 P 106270C (1968), copy submitted herewith) discloses only carboxylation reaction using carbon monoxide and oxygen.

Differences in Catalyst

The Examiner states that both prior art processes are closely related to each other with respect to sharing the transition metal during their respective processes. However, the Examiner's argument is illogical because the respective components other than the transition metal are completely different from one another in each catalyst.

That is, Asahi discloses a heteropoly acid catalyst whose skeleton having a deficient structural moiety in which a transition metal is incorporated. By contrast, Ichikawa uses a palladium carboxylate catalyst. Typically, one of ordinary skill in the art would not categorize a heteropoly catalyst as being a carboxylate compound. As discussed above, any motivation to combine Asahi with Ichikawa is lacking in view of such descriptions of the catalysts, since each catalyst is completely different from one another.

In this regard, the combination of palladium carboxylate with heteropoly acid or salts thereof (B1) is within the scope of the catalyst used in the present invention. However, heteropoly acid (B1) of the present invention differs from a compound in which a transition metal is incorporated into a heteropoly acid skeleton having deficient structural moiety. Therefore, the catalyst used in the present invention cannot result from the asserted combination of Asahi and Ichikawa. It is noted that the heteropoly acid (B1) of the present invention does not have deficient structural moiety, and consequently a transition metal is not incorporated therein.

Additionally, the Examiner states that the difference between the present invention and Asahi is that Asahi does not use carbon monoxide. It is further asserted that the catalyst of the present invention comprises the combination of a palladium compound catalyst (A) with catalyst (B), though Asahi uses a compound in which a transition metal is incorporated into a heteropoly acid skeleton having a deficient structural moiety.

Conclusion

It is, however, illogical to combine the references in an attempt to yield applicants' invention since each reference is directed to different substrates, catalysts, reaction schemes, and end products. As discussed above, no motivation exists which would permit such a combination, and the combination asserted by the Examiner is in conflict with the respective teachings of the cited references.

In view of the above, the Examiner fails to present a *prima facie* case of obviousness. The rejection under 35 USC 103(a) is without basis and should be withdrawn.

Should there be any outstanding matters that need to be resolved in the present application, the Examiner is respectfully requested to contact Raymond C. Stewart, Reg. No. 21,066 at the telephone number of the undersigned below, to conduct an interview in an effort to expedite prosecution in connection with the present application.

Payment in the amount of $110.00 is submitted herewith in connection with the requested one month extension of time.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37.C.F.R. §§1.16 or 1.14; particularly, extension of time fees.

Dated: April 30, 2007

Respectfully submitted,

By _____ #28,808 for

Raymond C. Stewart
Registration No.: 21,066
BIRCH, STEWART, KOLASCH & BIRCH, LLP
8110 Gatehouse Road
Suite 100 East
P.O. Box 747
Falls Church, Virginia 22040-0747
(703) 205-8000
Attorney for Applicant

Attachment: *Chem. Abstracts* 69 P 106270C (1968)

(Cl. 16 C 61); 28 Feb 1968, Appl. 30 Sep 1964; 2 pp. The title reaction with CO and O is effected in the presence of iodine and $FeCl_3$, VCl_3, $PdCl_2$, and (or) $PtCl_2$. Thus, a mixt. of 7.8 g. C_6H_6, 6.35 g. iodine, 0.5 g. $FeCl_3$, and 0.4 g. VCl_3 was charged in a 100-cc. autoclave, heated with 70 kg./cm.^{2} CO and 10 kg./cm.^{2} O at 250° for 2 hrs., and poured into 100 cc. 10% aq. NaOH. The mixt. was clarified and acidified to give BzOH in 18% conversion. Similar reaction of 9.2 g. PhMe at 200° with 6.35 g. iodine, 0.5 g. $PtCl_2$, and 0.4 g. VCl_3 gave *o*- and *p*-tolulc acid in 11.5% conversion. Ikuo Matsumoto

106271d Biphenyldicarboxylic acid. Rus'yanova, N. D.; Malyshova, N. V.; Yudina, A. G. U.S.S.R. 218,154 (Cl. C 07*c*), 17 May 1968, Appl. 14 Aug 1962; From *Izobret., Prom. Obraztsy, Tovarnye Znaki* 1968, 45(17), 31. The title compd. is prepd. by the oxidn. of phenanthrene with 12–40% AcOOH in the presence of Na hexametaphosphate and K pyrosulfate or a mixt. of these. NNCL

106272e 2,5-Dichloro-3-nitrobenzoic acid. Welch, Eldred (GAF Corp.) U.S. 3,397,229 (Cl. 260–515), 13 Aug 1968, Appl. 04 Dec 1963; 5 pp. 2,5-Dichlorobenzoyl chloride (I) is converted to 2,5-$Cl_2C_6H_3CO_2H$ (II); II is treated with a HNO_3–H_2SO_4 mixt. in oleum (62–67% SO_3 in 100% H_2SO_4), total H_2SO_4–II wt. ratio 3.3:1–4.5:1, total H_2SO_4–II molar ratio 6.5:1–8.8:1. Thus, 520 g. I is hydrolyzed (490 g. 90.6% H_2SO_4) to give II, 500 g. mixt. contg. 38% HNO_3 and 67% H_2SO_4 and 306 g. oleum contg. 65% SO_3 are added, and the mixt. (total H_2SO_4–II wt. ratio 3.33:1, total H_2SO_4–II molar ratio 6.5:1) is kept at 52–7° to give 65.0% (based on I) 2,5,3-$Cl_2(O_2N)C_6H_2CO_2H$, m. 215.7–18.6°, as compared to 63.0% for the control. BDFN

106273f Amino acids having useful pharmacological properties. Keberle, Heinrich; Faigle, Johann W.; Wilhelm, Max (CIBA Ltd.) Swiss 449,046 (Cl. C 07*c*), 11 Apr 1968, Appl. 09 Jul 1963; 8 pp. Amino acids $H_2NCH_2CH(p\text{-}XC_6H_4)CH_2CO_2H$ (I) are prepd. by redn. of the corresponding cyano, nitromethyl, iminomethyl, (α-aralkyl) aminomethyl, or carbobenzoyloxyaminomethyl derivs. Thus, a soln. of 2.1 g. β-cyano-*p*-chlorohydrocinnamic acid in 40 ml. EtOH and 5.5 ml. 2*N* HCl is hydrogenated over 150 mg. PtO_2 at room temp. and 1 atm. to give an aq. soln. of I.HCl (X = Cl). Addn. of 1*N* NaOH to pH 6–7 yields free I (X = Cl), m. 206–8° (H_2O). Similarly prepd. is I (X = Br), m. 228–9°. I have central retarding properties and are useful drug intermediates. E. Tobler

106274g Phenyl benzoate. Suchkov, V. V.; Sokolov, A. A.; Bark, D. S. (Experimental-Design Bureau of Synthetic Products) U.S.S.R. 221,685 (Cl. C 07*c*), 17 Jul 1968, Appl. 13 May 1966; From *Izobret., Prom. Obraztsy, Tovarnye Znaki* 1968, 45(22), 29. The title compd. is prepd. by treating PhOH with BzOH in the presence of $AlPO_4$ in an org. solvent, such as an excess of BzOH, at 230–40°. MSCL

106275h O-(Arylhydroxyacyl)-*N*-acyl-*N*-arylhydroxylamines. Baskakov, Yu. A.; Svirskaya, P. I.; Fadeeva, V. K. (All-Union Scientific-Research Institute for Chemicals for Plant Protection) U.S.S.R. 207,237 (Cl. C 07*c*), 22 Dec 1967, Appl. 23 May 1966; From *Izobret., Prom. Obraztsy, Tovarnye Znaki* 1968, 45(2), 22. To prep. the title physiol. active substances, *N*-acyl-*N*-arylhydroxylamines are treated with arylhydroxyalkanecarboxylic acid chlorides in org. solvent at −20° to +50°. MJCL

106276j Mono(β-hydroxyethyl) terephthalate. Fujito, Yasuhiro; Murakami, Tadateru (Mitsui Petrochemical Industries, Ltd.) Japan. 68 05,383 (Cl. 16 C 61), 28 Feb 1968, Appl. 26 Jan 1965; 2 pp. γ-Lactones contg. H_2O are good solvents for manuf. of the title compd. (I) from terephthalic acid (II) mono salt and ethylene oxide (III). Thus, a mixt. of II mono-K salt 20 and III 8.6 in 50% aq. γ-butyrolactone 160 parts was heated in an autoclave at 100° for 2 hrs. under 10 kg./cm.^{2} N to give 17.7 parts I, m. 178–80° (MeOH). The yield was 88% in 70% aq. γ-caprolactone. Ikuo Matsumoto

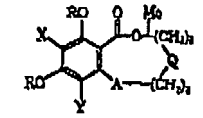
106277k Aromatic acid esters. Laboratorio Veris S.L. Span. 339,110 16 Jun 1968, Appl. 10 Apr 1967; 5 pp. High yields at low reaction temp. are obtained by adding 0.5 mole of an acid anhydride to a soln. of the alc. or phenol in $HCONMe_2$. Thus, to a stirred and cooled mixt. of 60 g. *iso*-PrOH in 200 ml. $HCONMe_2$ is added 112 g. Bz_2O in portions such that the temp. does not rise, and the mixt. warmed slightly for 0.5 hr. at 40°, dried over Na_2SO_4, and distd. in vacuo to give 155 g. *iso*-PrOBz. Similarly obtained were Ph acetylsalicylate, m. 109°, and benzyl cinnamate, m. 89°. F. B. Smith

106278m Bis(2-hydroxyethyl) benzenedicarboxylates. Bazant, Vladimir; Hetfleis, Jiri; Chvalovsky, Vaclav Czech. 125,599 (Cl. C 07*c*), 15 Dec 1967, Appl. 01 Apr 1966; 2 pp. Ethylene oxide (I) gives with terephthalic acid (II) and isophthalic acid (III) in Me_2SO products which are sufficiently pure for use in the manuf. of fibers. Carrying out the reaction to <90% conversion of the acid reduces the amt. of side products resulting from polymerization of I or etherification of the obtained esters. Thus, 22 g. I was passed at 600–845 mm. and 80° over 4 hrs. into a soln. of 60 g. II in 400 ml. Me_2SO, and the mixt. worked up to give 58 g. bis(2-hydroxyethyl) terephthalate, m. 109–10.5°. Another 6 g. was recovered from the mother liquors besides 14 g. 2-hydroxyethyl terephthalate. Similarly obtained were 135 g. bis(2-hydroxyethyl) isophthalate, m. 78–9°, and 12.8 g. 2-hydroxyethyl isophthalate from 100 g. III and 53 g. I. L. J. Urbanek

106279n Mono(β-hydroxyethyl) terephthalate. Fujita, Yasuhiro; Murakami, Tadateru (Mitsui Petrochemical Industries, Ltd.) Japan. 68 05,382 (Cl. 16 C 61), 28 Feb 1968, Appl. 26 Jan 1965; 2 pp. Cyclic ethers contg. H_2O are good solvents for manuf. of the title compd. (I) from terephthalic acid (II) mono salt and ethylene oxide (III). Disproportionation of the mono salt is prevented by the solvents. Thus, a mixt. of II mono-K salt 20 and III 8.6 in 50% aq. dioxane 160 parts was heated in an autoclave at 100° for 2 hrs. under 10 kg./cm.^{2} N, clarified while hot, and acidified to give 17.7 parts I, m. 178–80° (MeOH), acid no. 267. The yield was 73 and 68% in 50% aq. trioxane and 70% aq. tetramethylene formal, resp. Ikuo Matsumoto

106280f α,α-Dichloro-β,γ- and γ,γ-diphenyl-γ-butyrolactones. Lavrushin, V. F.; Pintova, L. N. U.S.S.R. 219,151 (Cl. C 07*c*), 17 May 1968, Appl. 14 Apr 1967; From *Izobret., Prom. Obraztsy, Tovarnye Znaki* 1968, 45(17), 20. The title compds. are prepd. by treating Cl_3CCO_2H with diaryl alkenes in the presence of $CuCl_2$ during boiling of the reaction mixt., with subsequent sepn. of the product. NNCL

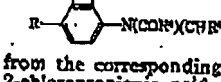
106281g Estrogenic compounds and animal growth promoters. Hodge, Edward B.; Hidy, Phil H.; Wehrmeister, Herbert L. (Commercial Solvents Corp.) U.S. 3,373,039 (Cl. 99–2), 12 Mar 1968, Appl. 29 Jun 1966-26 Oct 1967; 7 pp. The compds. of this invention (I) exhibit estrogenic activity or aid in increasing the rate of growth in meat-producing animals, e.g., cattle, lamb, and swine. A mixt. of 10 g. I (R = Me, X = H, Y = H, A = CH:CH, Q = CO) and 100 ml. cold coned. HNO_3 was stirred 2 hrs. to effect soln., poured over cracked ice, and filtered to give 3.7 g. I (R = Me, X = H, Y = NO_2, A = CH:CH, Q = CO), m. 163–4° (MeOH). Similarly prepd. was I (R = H, X = H, Y = NO_2, A = CH:CH, Q = CO) (Ia), m. 206–8°. A mixt. of 5.0 g. I (R = H, X = H, Y = H, A = CH_2CH_2, Q = CHOH) in 150 ml. AcOH was slowly added to 10 ml. cold coned. HNO_3, stirred 1 hr., poured into 1 l. H_2O, and refrigerated



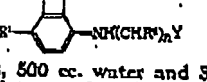
(I)

to give I (R = H, X = Y = NO_2, A = CH_2CH_2, Q = CHOH), m. 179–82°. Similarly prepd. was I (R = H, X = Y = NO_2, A = CH_2CH_2, Q = CO), m. 101–7°, and the 3,5-dinitrodeoxytetrahydro deriv. (Ib) of I (R = H, X = Y = H, A = CH:CH, Q = CO). A mixt. of 50 ml. coned. (95%) H_2SO_4, 1.5 g. Ib, and 0.5 g. KNO_3 was stirred 1 hr. in an ice bath, poured into 500 ml. H_2O, and refrigerated to give Ia. Ia (2 g.) in 150 ml. EtOH was catalytically reduced at room temp. in the presence of 0.5 g. 5% Pd/C at 50 psi. H 3 hrs. to give I (R = H, X = H, Y = NH_2, A = CH_2CH_2, Q = CO), m. 185–90°. The following I were similarly prepd. (R, X, Y, A, Q, and m.p. given): Me, H, NH_2, CH_2CH_2, CO, 139–44°; H, H, NH_2, CH_2CH_2, CHOH, 258–65°. Also prepd. was the 3,5-diaminodeoxytetrahydro analog of Ib. Ia (2 g.) was reduced as above, the reaction mixt. treated with 1.5 ml. HCHO, catalytic redn. continued 3 hrs., the mixt. filtered, the filtrate evapd. to dryness, and the residue crystd. from EtOH to give I (R = H, X = H, Y = Me_2N, A = CH_2CH_2, Q = CHOH). A mixt. of 20 g. Ib in 20 ml. coned. HNO_3 was stirred 2 hrs., treated with 200 ml. cold H_2O, and worked up in the usual manner to give I (R = H, X = NO_2, Y = H, A = CH:CH, Q = CO), m. 147–50°. The filtrate from the latter yielded Ia. Formulations for pelleted rations contg. the above compds. as active ingredients are given. I. Levi

106282h Wild oat herbicides. Shell Internationale Research Maatschappij N.V. Neth. Appl. 67 17,715 (Cl. C 07*c*), 01 Jul 1968, Appl. 26 Oct 1967; 20 pp. Title compds. (I) were prepd.



(II)



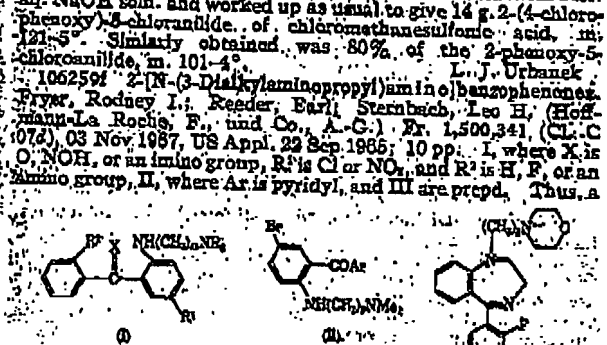
(III)

from the corresponding II. Thus, 500 cc. water and 3000 g. 2-chloropropionic acid were added to a soln. of 2686 g. 3,4-dichloroaniline in 8400 cc. *iso*-PrOH. The mixt. was heated to 40°, 5600 g. $NaHCO_3$ added, and the mixt. refluxed 113 hrs., cooled, poured into 100 l. water, filtered, acidified with HCl to pH 3–4, and filtered. The ppt. was washed and dried to give 2455 g. *N*-(3,4-dichlorophenyl)alanine (III), m. 148–9°. A soln. of 2475 g. III in 10 l. abs. EtOH was refluxed 6 hrs., while passing gaseous HCl, and kept overnight to give 2170 g. II (R^1 = R^2 = Cl, R^3 = R^4 = H, n = 2, Y = CO_2Et) (IV), m. 37–8°. IV refluxed 4 hrs. with 1450 g. BzCl in anhyd. benzene, and another 20 hrs. with 290 g. addnl. BzCl to give 2220 g. I (R^1 = R^2 = Cl, R^3 = R^4 = H, R^1 = Ph, n = 2, Y = CO_2Bt), m. 50–2°. Similarly prepd. were the following I (R^1 = R^3 = Cl, R^2 = R^4

2007年 3月19日 10時05分 後藤特許事務所 NO. 4548 P. 5

between $ClSO_2CH_2Cl$ (I) and aromatic amines in a mixt. of pyridine and aromatic chlorinated hydrocarbon reduces decompn. side reactions and permits the use of tech. grade reactants. Thus, 12.7 g. 4,4'-dichloro-2-aminodiphenyl ether in 50 ml. dry PhCl and 5 ml. pyridine was treated in 2 hrs. with 9 g. I, and the mixt. stirred 1 hr. and kept 12 hrs. The product was extd. with 0.2*N* aq. NaOH soln. and worked up as usual to give 14 g. 2-(4-chlorophenoxy)-5-chloranilide of chloromethanesulfonic acid, m. 121–5°. Similarly obtained was 80% of the 2-phenoxy-5-chloranilide, m. 101–4°. L. J. Urbanek

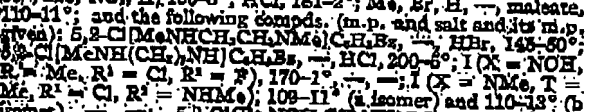
106259f 2-[*N*-(3-Dialkylaminopropyl)amino]benzophenones. Fryer, Rodney I.; Reeder, Earl J.; Sternbach, Leo H. (Hoffmann-La Roche, F., und Co., A.-G.) Fr. 1,500,341, (Cl. C 07d), 03 Nov 1967, US Appl. 22 Sep 1965; 10 pp. I, where X is O, NOH, or an imino group, R^1 is Cl or NO_2, and R^2 is H, F, or an amino group, II, where Ar is pyridyl, and III are prepd. Thus, a



(I) (II) (III)

mixt. of 200 ml. $H_2N(CH_2)_3NH_2$, 104 g. 2,5-Cl(O_2N)C_6H_3Br, and 900 ml. pyridine is refluxed 3 hrs. to give 2-(3-aminopropylamino)-5-nitrobenzophenone, m. 97–8°; HCl salt m. 239–40°. Similarly, 5,2-Cl(*p*-$MeC_6H_4SO_2NH$)C_6H_3Br is treated with $Me_2N(CH_2)_3Cl$ to give 5-chloro-2-[*N*-(3-dimethylaminopropyl)-*p*-toluenesulfonamido]benzophenone, m. 103–6°, which is heated with H_2SO_4 to give I (X = O, R = Me, R^1 = Cl, R^2 = H).HCl, m. 157–63°. I (X = O, R = R^2 = H, R^1 = Cl).HCl (m. 170°) is prepd. from 5,2-Cl[Cl(CH_2)$_3$NH]C_6H_3Br and NH_3. Also prepd. according to the above and related methods, are the following I (X = O) (R or NR_2, R^1, R^2, m.p., and salt and its m.p. given): piperidino, H, H, —, HCl, 202–10°; Me, NO_2, H, —, HCl, 180–1°; Me, Cl, F, 170–1°, HCl, 172–4°; Me, Cl, $MeNH_2$, 85–7°, —, —; Et, Cl, F, —, HCl, 144–7°; Me, Cl, H, —, HCl, 157–63°; piperazino, Cl, F, —, dimaleate, 157–9°; 4-methylpiperazino, Cl, F, —, dimaleate, 185–8°; 4-(2-hydroxyethyl)piperazino, Cl, F, —, dimaleate, 166–7°; 4-(2-vinyloxyethyl)piperazino, Cl, F, —, dimaleate, 140–2°; 4-(2-ethoxyethyl)piperazino, Cl, F, —, dimaleate, 153–5°; morpholino, Cl, F, —, HCl, 148–50°; Me, NO_2, H, 105–6°, HCl, 181–2°; Me, Br, H, —, maleate, 110–11°; and the following compds. (m.p. and salt and its m.p. given): 5,2-Cl[$MeNHCH_2CH_2NMe$]C_6H_3Br, —, HBr, 145–50°; 5,2-Cl[$MeNH(CH_2)_3NH$]C_6H_3Br, —, HCl, 200–5°; I (X = NOH, R = Me, R^1 = Cl, R^2 = F), 170–1°, —, —; I (X = NMe, T = Me, R^1 = Cl, R^2 = NHMe), 109–11° (a isomer) and 110–13° (b isomer), —, —; 5,2-Cl($Et_2NCH_2CH_2NH$)C_6H_3Br, —, HCl.0.5H_2O, 197–9°; II (Ar = 4-pyridyl), —, maleate, 151–2°; II (Ar = 2-pyridyl), —, 2HCl.0.5H_2O, 177–85° (decompn.); 5,2-F,C($Me_2NCH_2CH_2NH$)C_6H_3Bz, —, HCl, 203–5°; 5,2-Cl[Cl(CH_2)$_3$NH]C_6H_3Bz, 60–3°, —, —; 5,2-Cl($Et_2NHCH_2CH_2NH$)C_6H_3Bz, 84–6°, —, —; 5,2-Cl($Et_2NHCH_2CH_2NH$)COC_6H_4F-*p*, —, HCl, 205–25°; 2'-benzoyl-4'-chloro-*N*-(3-bromopropyl)-*p*-toluenesulfonanilide, 104°, —, —; 2'-benzoyl-4'-chloro-*N*-(3-dimethylaminopropyl)-*p*-toluenesulfonanilide, 99–104°, —, —. BDPF

106260z Methylenediphloroglucinols. Andersen, Lars; Penttila, Aseli; Sundman, Jacobus (Oesterbottic Medica AB) Finn. 36,704, (Cl. C 07c), 30 Nov 1967, Appl. 15 May 1964; 3 pp. Methylenediphloroglucinol derivs. (I) were prepd. by combining acylfilicinic acid (II) through a methylene bridge with 4,2,6-MeO(HO)$_2C_6H_2COPr$ (III) in water or org. solvent in the presence of alk. catalyst at 20°. For example, 2 g. propanylfilicinic acid

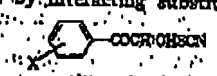


(I) (II)

and 2 g. III were dissolved in 40 ml. MeOH and 0.8 ml. CH_2O and 0.5 ml. piperidine were added. The mixt. was kept 20 hrs., and 10 ml. water was added to yield desaspidin PB, I (R = Et), m. 141–2°. Similarly prepd. were I (R and m.p. given): Bu, 123–5°; n-C_5H_{11}, 105–6°; iso-Pr, 133–5°. Jaakko E. Nilio-Rama

106261a 2-Hydroxy-4-alkoxybenzophenones. Curvich, Ya. S.; Lebedev, S. S.; Solodar, L. S.; Mikhailov, V. V. U.S.S.R. 218,144 (Cl. C 07c), 17 May 1968, Appl. 18 Jan 1964; From *Izobret., Prom. Obraztsy, Tovarnyx Znaki* 1968, 45(17), 19. The prep. the title compds. with a C_4 or higher alkyl group, the ethers of resorcinol were condensed with BzCl in the presence of $AlCl_3$. NNCL

106262b Substituted β-thiocyanatovinyl aryl ketones. Savenkov, N. F.; Khokhlov, P. S.; Blizmyuk, N. K. (All-Union Scientific Research Institute of Phytopathology) U.S.S.R. 218,143 (Cl. C 07c), 17 May 1968, Appl. 03 Apr 1967; From *Izobret., Prom. Obraztsy, Tovarnyx Znaki* 1968, 45(17), 19. Title compds. of the formula I where X is Cl, Br, F, Me, or NO_2, are prepd. by interacting substituted β-chlorovinyl aryl



(I)

ketones with thiocyanate salts in a polar org. solvent at 10–100°, preferably at 20–50°. NNCL

106263c Benzophenones. Dobratz, Elmer H.; Kolka, Alfred J. (Koppers Co., Inc.) U.S. 3,403,183 (Cl. 260–591), 24 Sep 1968, Appl. 16 Dec 1966; 6 pp. Polyhydroxy- and alkoxybenzophenones were prepd. by condensing hydroxy- or alkoxy-substituted benzenes with BzOH or a hydroxy or alkoxy deriv. in the presence of a catalyst-solvent (HF) system. The HF was removed and the residue treated in a soln. of pH 9–10 with Na dithionite, followed by adjusting the pH to 7.5–8.9 to obtain a pure and undiscolored benzophenone ppt. The compds. are useful in the prepn. of dyes, resins, and uv light absorbers. Thus, resorcinol 55.1, BzOH 66.0, and anhyd. HF 170.1 g. was mixed to form a pale-yellow soln., and the soln. was placed in a precooled autoclave and heated to 75° over 15 min. and kept at 75° for 4 hrs. The autoclave and contents were cooled in an ice bath and the dark, red-yellow soln. from the autoclave was poured into a polyethylene container. HF was removed by distn., dil. HCl was added with stirring, and a finely granulated product ppt., filtered, and washed with dil. acid and water to give a pale-yellow to brown granular solid. To the product 3.8 g. tartaric acid, 35 g. Na_2CO_3, and 450 ml. H_2O were added. The mixt. was stirred and heated to 90° to dissolve all the solid and give a dark-brown soln. with evolution of CO_2. The soln. was cooled to 75°, and 2.3 g. Na dithionite was added to give a pale-orange soln., which was stirred at 70–5° for 0.5 hr. and cooled to 45°, and dil. H_2SO_4 added dropwise to a pH of 3.45 to give a fine cryst. white product, 99% pure 2,4-dihydroxybenzophenone. Similarly prepd. were 4,4'-dihydroxybenzophenone, m. 209–14°, 88.2% yield, 2,4,4'-trihydroxybenzophenone, and 2,4'-dihydroxybenzophenone, m. 146–7°. BRPN

106264d Purification of sodium salicylate. Pechcidt, Jiri; Tichy, Zdenek; Blasek, Jan Czech. 125,497 (Cl. C 07c), 15 Dec 1967, Appl. 28 Jul 1965; 2 pp. Salicylic acid (1000 kg.) is dissolved at 60° in a 40–2% soln. of 285 kg. NaOH in demineralized water and the soln. is stirred 1 hr., then 30 min. with 25 kg. C, filtered, and spray dried at 180–220° at a contact period of <5 sec. The short exposure to heat prevents formation of resinous by-products, encountered in the cryst. process. L. J. Urbanek

106265e p-Hydroxybenzoic acid. Yasuhara, Hiroshi; Nogi, Tatsuo (Toyo Rayon Co., Ltd.) Japan. 68 11,211 (Cl. 16 C 624), 11 May 1968, Appl. 18 Mar 1966; 2 pp. A mixt. of 20 g. PhOK, 21 g. K_2CO_3, and 70 g. Ph_2O in an autoclave is heated 4 hrs. at 240° with 50 kg./cm.^{2} CO, 100 ml. H_2O added, the reaction mixt. washed with Et_2O, the aq. phase adjusted to pH 9 and washed with Et_2O, and 12*N* HCl added to give 17.5 g. title product. The use of naphthalene instead of Ph_2O is also described. Hiroshi Kataoka

106266f p-tert-Butylbenzoic acid. Kimura, Ryuichi; Yabuuchi, Takahiro; Murakami, Hirotaka; Nishiwaki, Yoshihiro (Research Foundation for Practical Life) Japan. 68 11,444 (Cl. 16 C 61), 14 May 1968, Appl. 02 Dec 1964; 3 pp. Into a hot (140°) mixt. of 856 g. *p*-*tert*-butyltoluene, 8.56 g. Co naphthenate, 10 cc. tetrabromoethane, and 20 cc. tetrachloroethylene O is introduced at 200 l./hr. for 8 hrs. to give 480 g. title product, m. 163–5°. Hiroshi Kataoka

106267g p-tert-Butylbenzoic acid. Kimura, Ryuichi; Yabuuchi, Takahiro; Murakami, Hirotaka; Nishiwaki, Yoshihiro (Research Foundation for Practical Life) Japan. 68 11,445 (Cl. 16 C 61), 14 May 1968, Appl. 02 Dec 1964; 3 pp. *p*-*tert*-Butyltoluene was oxidized in a mixt. of Co naphthenate, tetrabromoethane, and tetrachloroethylene with O at 80–98°. Hiroshi Kataoka

106268h p-tert-Butylbenzoic acid. Kimura, Ryuichi; Hara, Tadashi; Yabuuchi, Takahiro (Research Foundation for Practical Life) Japan. 68 11,210 (Cl. 16 C 61), 11 May 1968, Appl. 30 Jul 1964; 2 pp. The Me group of *p*-*tert*-butyltoluene (I) is selectively oxidized to manuf. the title compd. (II). In an example, dry air contg. a small amt. of ozone is introduced at 200 l./hr. into a hot (90°) mixt. of 1 kg. I, 3 l. AcOH, 30 g. Co acetate, and 30 g. tetrachloroethylene to give 965 g. II, m. 163–5°. Hiroshi Kataoka

106269j Stereoisomeric 2-phenylcyclopropylamides of 2-phenylcyclopropanecarboxylic acids. Levina, R. Ya.; Bolesov, I. G.; Suzmina, L. S. U.S.S.R. 202,925 (Cl. C 07c), 28 Sep 1967, Appl. 28 Jun 1966; From *Izobret., Prom. Obraztsy, Tovarnyx Znaki* 1967, 44(20), 33. The title physiol. active compds. are prepd. by treating *cis*- or *trans*-2-phenylcyclopropylamine with *cis*- or *trans*-2-phenylcyclopropanecarboxylic acid chloride in the presence of an alkali hydroxide. The final product is recovered by a known technique. MGCL

106270c Carboxylation of benzene and toluene. Komatsu, Hideo; Kato, Tadao (Toyo Rayon Co., Ltd.) Japan. 68 05,881